

Sulfate Attack on Blended Portland Cements

By A. Borsoi, S. Collepardi, L. Coppola, R. Troli, and M. Collepardi

Synopsis: Paste and mortar specimens were manufactured by using ordinary portland cement (OPC), C₃A-free portland cement, slag cement and pozzolan cement. A carbonaceous or siliceous filler (10% by cement weight) was blended with each of the above portland cements. Limestone or quartz sands were used for mortar mixtures. Four different water-cement ratios (*w/c*) were adopted: 0.55, 0.50, 0.45, and 0.40.

After a 28-day wet curing, paste and mortar specimens were immersed in MgSO₄ aqueous solutions with a SO₄⁻ concentration of 350, 750, and 3000 mg/l, corresponding to chemically aggressive exposures 5a, 5b, and 5c respectively, according to the European Norms (ENV 206).

The deterioration of cement paste specimens was studied by X-ray diffraction analysis to detect ettringite and/or thaumasite formation in relationship with the visual observation of sulfate attack.

The deterioration of mortar specimens was studied by measuring elastic modulus and compressive strength at different periods of aggressive exposure (from 1 month to 5 years).

After 5 years of exposure to the sulfate attack, paste and mortar specimens with slag and pozzolan cements were undamaged independent of the sulfate concentration, sand type, and *w/c*.

On the other hand, paste and mortar specimens with blended limestone-portland cements showed surface damage when exposed to the 3000 mg/l of SO₄⁻ aqueous solution. However, they did not show loss of either compressive strength or elastic modulus in the 5 years of sulfate exposure. The surface damage was mitigated when OPC was replaced by the C₃A-free portland cement and completely eliminated when this cement was blended with a siliceous filler rather than with a limestone case.

Thaumasite and ettringite are responsible for the surface attack. The amount of thaumasite was a little higher in the presence of blended limestone portland cement.

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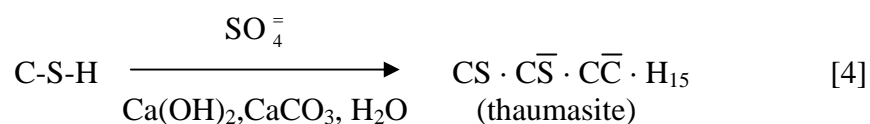
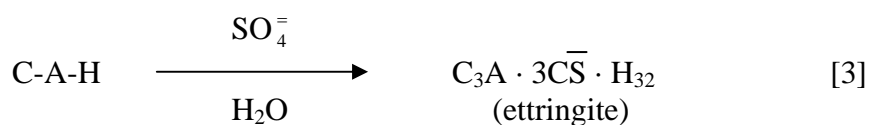
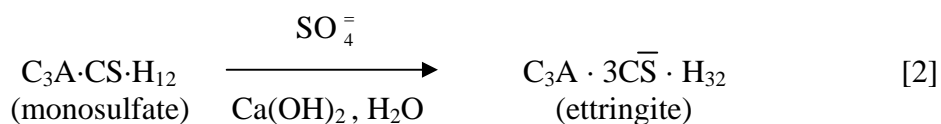
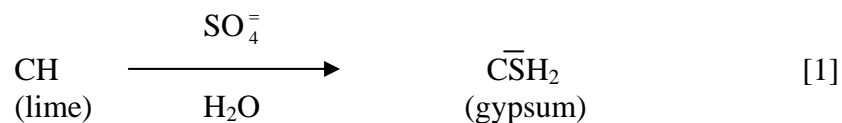
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INTRODUCTION

Concrete exposed to environmental sulfate can be damaged due to the formation of gypsum, ettringite, and thaumasite as a result of chemical interaction with the portland cement hydration products, such as calcium hydroxide (CH), monosulfate ($C_3A \cdot \bar{C}\bar{S} \cdot H_{12}$), calcium aluminate-hydrates (C-A-H), and calcium-silicate-hydrates (C-S-H):



where \overline{CS} and \overline{CC} indicate CaSO_4 and CaCO_3 respectively. In general, damaging effects related to ettringite formation appear in form of expansion, spalling and cracking, whereas thaumasite formation, favored by low temperatures (5-10°C), and gypsum formation cause strength reduction and mass loss (2, 3).

Both ettringite and thaumasite can be detected by X-ray diffraction (XRD) analysis. However, their XRD patterns are very similar and only through the most sophisticated equipments can be distinguished, particularly when both the products are present in sulfate-damaged concrete structures. Therefore, one cannot exclude that in many case histories published in the past literature, thaumasite and ettringite rather than ettringite alone were responsible for the sulfate attack.

PURPOSE OF THE STUDY

As far as concrete composition is concerned, there are two strategies to produce durable concretes exposed to sulfate attack:

- i)* to adopt a low water-cement ratio (w/c) for making a low-porosity, impermeable concrete to reduce the sulfate penetration from the environment into concrete;
- ii)* to select a cement which by itself should be able to resist the sulfate attack.

Additional and important requirements for durable concretes are adequate compaction of fresh concrete and proper curing of de-molded structures to reduce macrovoids and capillary pores, respectively.

According to ACI recommendations (4), European norms (5), and Japanese standards (6) the adoption of a relatively low w/c (for instance: 0.55-0.50) is adequate to manufacture durable concretes exposed to environments with moderate sulfate concentrations (for instance: $\text{SO}_4^- < 1000$ mg/l in water). However, for environments with higher sulfate contents (for instance: $\text{SO}_4^- > 3000$ mg/l) a lower w/c (0.50-0.45) should be adopted in combination with a sulfate-resisting cement.

Typical sulfate-resisting cements are considered to be:

- low- C_3A portland cements such as Type V according to ASTM specification;
- blended portland cements containing pozzolan or slag.

However, C_3A -free portland cements, as well as pozzolan or slag-blended cements, are potentially vulnerable in a sulfate-rich environment since $C-S-H$ (even in the absence of $C-A-H$) can be transformed into thaumasite according to the equation [4] shown above. One purpose of the present paper is to determine

whether or not C_3A -free portland cement and pozzolan or slag-blended cements are really sulfate-resisting particularly in cold-temperature conditions (5°C) favoring the thaumasite formation.

A second purpose of the present study was to assess whether or not limestone-blended cements, which are produced in agreement with EN 197/1 standard specification (7) and widely used in Europe, are prone to thaumasite formation. Particularly in UK (8) there are serious concerns on the use of limestone-blended cements for concrete structures exposed to sulfate attack. In fact, as shown by equation [4], the presence of limestone in the form of fine CaCO_3 powder in these cements*, could favor the thaumasite-related damage in concrete structures.

MATERIALS AND METHODS

Raw materials. Table 1 shows the chemical composition and the fineness of the raw materials. Two portland cements were used: one was a low- C_3A portland cement (LCPC) with zero- C_3A content; the other was an ordinary portland cement (OPC) with 8.2% C_3A content. Fly ash (FA) and ground granulated blast-furnace slag (S), limestone (L) in form of calcite, and quartz (Q) were used to produce blended cements.

Cements. Table 2 shows the composition of the six cements examined in the present work. Blended limestone-portland cements (OPC-L and LCPC-L) were produced by mixing ground limestone (10%) with OPC or LCPC. For comparison purpose, the limestone-portland blended cements were related to other blended cements where the limestone powder was replaced by the same amount (10%) of a pure quartz powder (OPC-Q and LCPC-Q, respectively). Pozzolan or slag-portland cements were obtained by mixing OPC with fly ash (30%) or slag (50%), respectively: these blended cements are indicated as FA-PC or S-PC respectively.

Sands. Two sands were used, both with a fineness modulus of 2.6 and maximum size of 4 mm, the difference being the mineralogical nature: limestone ($\text{CaCO}_3 > 99\%$) or quartz ($\text{SiO}_2 > 98\%$).

Mortar mixtures. Table 3 shows the combinations of each cement with sand (limestone or quartz type) as adopted in the present study. Mortar mixtures with a sand-cement ratio of 3:1 were manufactured instead of concrete mixtures in order to accelerate the sulfate attack on the cement matrix.

The limestone sand was used for mortars with blended limestone-portland cements (LCPC-L and OPC-L), whereas the quartz sand was used for mortars with portland cements blended with the quartz filler (LCPC-Q and OPC-Q).

* According to EN 197/1 the limestone content is in the range of 6-20% for CE II A/L and 21-35% for CE II B/L.

This combination was helpful for a better understanding of the role played by CaCO_3 in the thaumasite formation, if any, and related damage of specimens.

Pozzolan and slag portland cement (FA-PC and S-PC respectively) were mixed with either limestone or quartz sand.

For the manufacture of mortar prisms (40x40x160 mm) each combination of the cement-sand system (Table 3) was mixed with water according to the following water-cementitious material ratio (w/cm^{**}): 0.55, 0.50, 0.45, and 0.40.

Mortar specimens were cured at 20°C for 28 days before exposure to sulfate attack.

Cement pastes. Neat cement paste specimens with the above w/cm (0.55, 0.50, 0.45, and 0.40) were also manufactured and exposed to the same environmental sulfate attack. Neat cement paste specimens were more suitable than mortar specimens for detecting ettringite and thaumasite by X-ray diffraction (XRD) analysis.

Exposure to sulfate attack. Cement paste and mortar specimens were immersed at 5°C in MgSO_4 aqueous solutions with a SO_4^{2-} content of 350, 750, 3000 mg/l corresponding to chemically aggressive exposure classes 5a, 5b, and 5c respectively according to ENV 206 (5). A temperature as low as 5°C was selected because thaumasite formation is favored by low temperatures (1).

Methods. Mortar specimens were monitored by measuring dynamic elastic modulus (through ultrasonic pulse velocity test) and compressive strength as well as by visual observation. Figure 1 shows four typical visual rates of mortar and paste specimens: from A (sound specimen) to D (specimen with surface microcracks or mass loss).

Cement paste specimens were used to detect ettringite and thaumasite by XRD analysis in relation with some specific visible damage on the surface of the specimens.

RESULTS

Visual rating of the sulfate attack. Figures 2 and 3 show the deterioration process, in terms of visual rating, of mortar specimens ($w/cm = 0.40$) with limestone and quartz sand respectively. These results refer to the MgSO_4 solution with 3000 mg/l. No significant visible damage was detected with lower sulfate concentrations (350 or 750 mg/l). Damages with higher w/cm were a little more severe but always related to the specimen surface only.

** Cementitious material (cm) indicates the mass of cement plus filler (limestone or quartz), fly ash or slag.

Figure 2 indicates that, in the presence of limestone sand, mortar specimens with blended limestone-portland cements start to deteriorate after about 2.5 years. The surface of mortar specimens with OPC-L is severely damaged (visual rating = *D*) in about 4.5 years. The use of C₃A-free portland cement (LCPC-L) slightly mitigates the final surface damage (visual rating *C* instead of *D*). In the presence of fly ash (FA-PC) or slag cement (S-PC), no damage is visually recorded within the studied exposure time (5 years).

When the carbonaceous filler and limestone sand are replaced by the corresponding siliceous materials, the sulfate attack appears to be slightly mitigated (Fig. 3): in particular, the final visual rating of the surface damage becomes *C* (Fig. 3) instead of *D* (Fig. 2) when OPC is used. The excellent performance (no damage) of fly ash or slag portland cement (FA-PC or S-PC respectively) is confirmed even when a siliceous sand is used (Fig. 3).

Similar results were obtained for cement paste specimens (Fig. 4 and 5).

Elastic modulus and compressive strength. Measurements of elastic modulus or compressive strength were unable to show any significant change in the mechanical properties of the mortar specimens within 5 years of sulfate exposure time under the specific laboratory conditions adopted in this work, with all cement types used in this study, including the portland-limestone blended cements. Figures 6 and 7 show examples of elastic modulus and compressive strength measurements as a function of exposure time to sulfate attack.

On the other hand, the damage – as detected by visual observation – deals, if any, with the skin of the specimens and then causes only negligible changes in properties – such as elastic modulus or compressive strength – related to the whole mass of the specimens. However in real concrete structures the sulfate attack can become more severe because of microcracks (caused by restrained thermal and drying shrinkage or loading in service) which favor a deeper penetration of sulfate into the cement matrix (9).

XRD analysis. Figures 8-13 indicate some XRD patterns of cement paste specimens before and after (43 months) the exposure to the sulfate environment ($\text{SO}_4^{2-} = 3000 \text{ mg/l}$). The analyzed sample was taken from the surface (1-mm deep) of the specimens. Neither ettringite nor thaumasite can be detected (except the small amount of ettringite early formed as set regulator) in specimens without any visible damage which were manufactured with FA-PC (Fig. 8), S-PC (Fig. 9) or LCPC-Q, i.e. the C₃A-free portland cement blended with the siliceous filler (Fig. 10). Thaumasite and ettringite formed in specimens with visible damages (Fig. 11-13): the thaumasite peak appears to be higher than that of ettringite in specimens with OPC (Fig. 11) or C₃A-free portland cement (Fig. 12) both blended with 10% limestone powder, whereas it is lower in the specimen with OPC and siliceous filler (Fig. 13).

After an exposure time of 43 months to the sulfate attack the peak of calcium hydroxide (CH), produced by portland cement hydration, was detected in all the

un-damaged specimens (Fig. 8-10). However, the amount of CH was lower in FA-PC (Fig. 8) or S-PC (Fig. 9) paste specimens due to the combination of fly ash or slag respectively with calcium hydroxide (pozzolanic activity).

In the damaged specimens (Fig. 11-13) no CH was detected by XRD after an exposure of 43 months to the sulfate attack. The consumption of CH is related to the formation of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by reaction [1] with sulfate ions.

However, gypsum was not detected by XRD since it was consumed to feed the ettringite or thaumasite formation according to the process [3] or [4] respectively.

CONCLUSIONS

1. Paste and mortar specimens with fly ash and slag blended cements were not damaged within 5 years of exposure to MgSO_4 aqueous solutions independent of the experienced w/cm (0.55-0.40), the sand type (carbonaceous or siliceous), and the sulfate concentration (350-3000 mg/l).
2. Paste and mortar specimens with blended limestone-portland cements showed surface damage when exposed to a 3000 mg/l SO_4^- aqueous solution of MgSO_4 . However, they did not show loss of either compressive strength or elastic modulus in the 5 years of sulfate exposure.
3. The above surface damage was mitigated when OPC was replaced by a C_3A -free portland cement and completely eliminated when this cement was blended with a siliceous filler rather than with a limestone one.
4. Thaumasite and/or ettringite are responsible for the surface attack. The amount of thaumasite was a little higher in the presence of blended limestone-portland cements.

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Table 1 – Chemical composition and fineness of raw materials

Oxide composition (%)	Ordinary portland cement (OPC)	Low-C ₃ A portland cement (LCPC)	Fly ash (FA)	Slag (S)	Limestone (L)	Quartz (Q)
SiO ₂	19.90	20.59	36.50	59.94	-	99.9
Al ₂ O ₃	4.57	3.66	11.67	22.87	-	-
CaO	63.82	63.78	38.95	3.08	-	-
Fe ₂ O ₃	2.36	6.10	1.01	4.67	55.0	-
MgO	1.15	0.95	8.08	1.55	-	-
SO ₃	0.74	0.48	0.42	2.19	-	-
K ₂ O	0.90	0.26	0.34	0.62	-	-
Na ₂ O	3.30	2.50	0.00	0.35	-	-
L.O.I.	-	-	-	-	43.2	-
C ₃ A	8.20	0.00	-	-		
Blaine fineness (cm ² /g)	4050	4010	3990	4090	4050	4030

Table 2 - Composition of cements.

Cement	Ingredients:					
	OPC	LCPC	FA	S	L	Q
OPC-L	90	-	-	-	10	-
OPC-Q	90	-	-	-	-	10
LCPC-L	-	90	-	-	10	-
LCPC-Q	-	90	-	-	-	10
FA-PC	70	-	30	-	-	-
S-PC	50	-	-	50	-	-

Table 3 – Percentages of cement and sand in each mortar mixture.

Mortar Mix	Cements (%)						Sand (%)	
	OPC-L	OPC-Q	LCPC-L	LCPC-Q	FA-PC	S-PC	L	Q
OPC-L/L	25	-	-	-	-	-	75	-
OPC-Q/Q	-	25	-	-	-	-	-	75
LCPC-L/L	-	-	25	-	-	-	75	-
LCPC-Q/Q	-	-	-	25	-	-	-	75
FA-PC/L	-	-	-	-	25	-	75	-
FA-PC/Q	-	-	-	-	25	-	-	75
S-PC/L	-	-	-	-	-	25	75	-
S-PC/Q	-	-	-	-	-	25	-	75

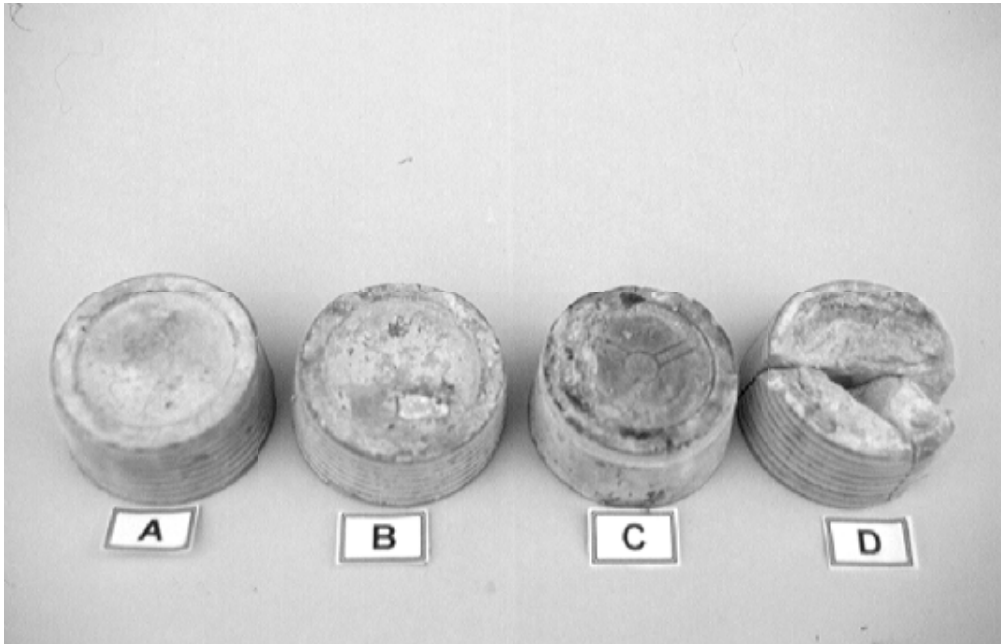
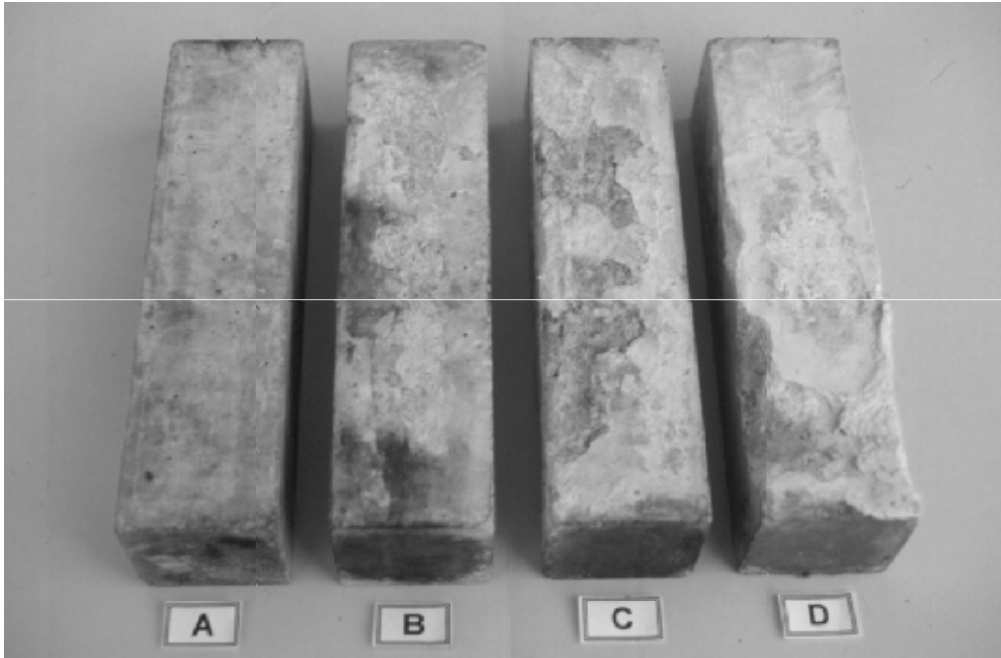


Fig. 1 - Typical mortar (above) and paste (below) specimens after gradual and increasing surface damage from A (sound) to D.

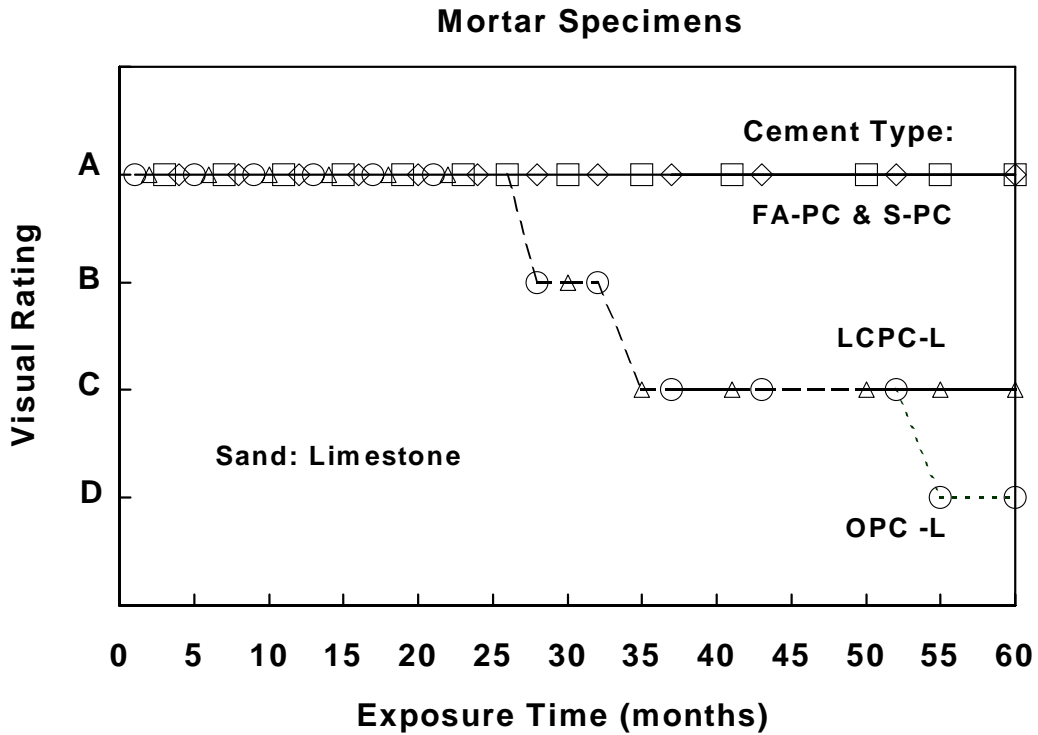


Fig. 2 – Surface damage by sulfate attack of mortar specimens , with limestone sand, as a function of cement type (w/cm = 0.40).

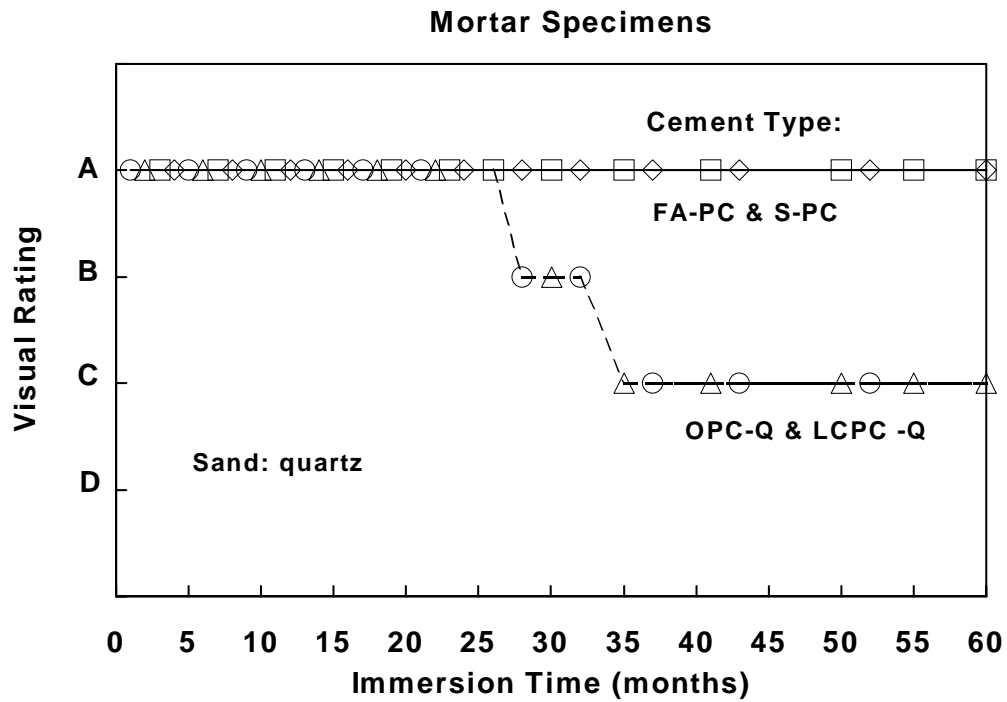


Fig. 3 - Surface damage by sulfate attack of mortar specimens , with quartz sand, as a function of cement type (w/cm = 0.40).

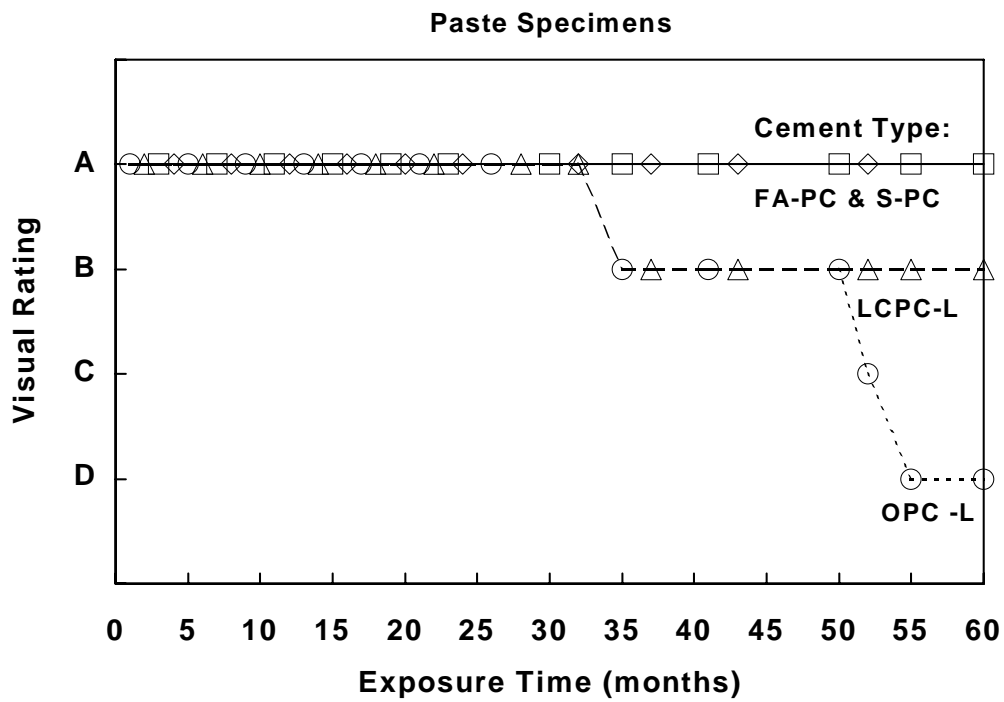


Fig. 4 - Surface damage by sulfate attack of cement paste specimens as a function of cement type ($w/cm = 0.40$).

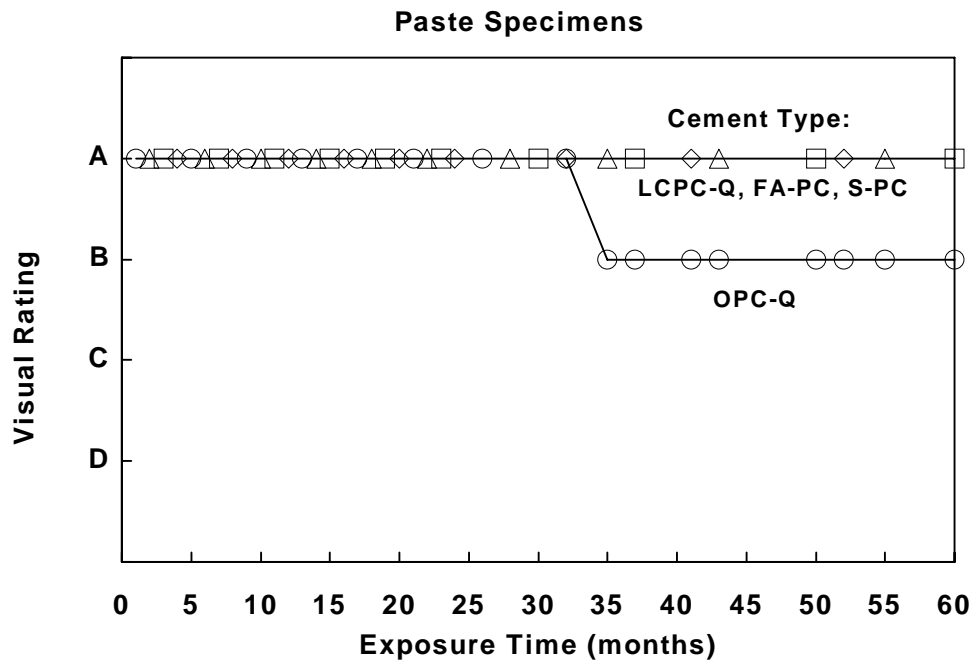


Fig. 5 - Surface damage by sulfate attack of cement paste specimens as a function of cement type ($w/cm = 0.40$).

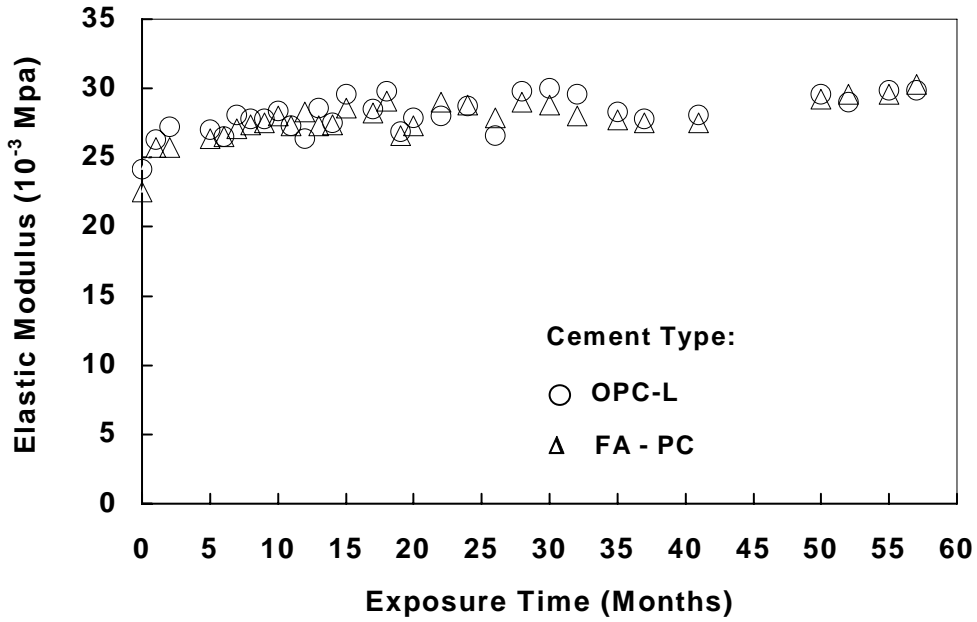


Fig. 6 – Elastic modulus of mortar specimens ($w/cm = 0.55$), with limestone sand, as a function of cement type ($SO_4^- = 3000$ mg/l).

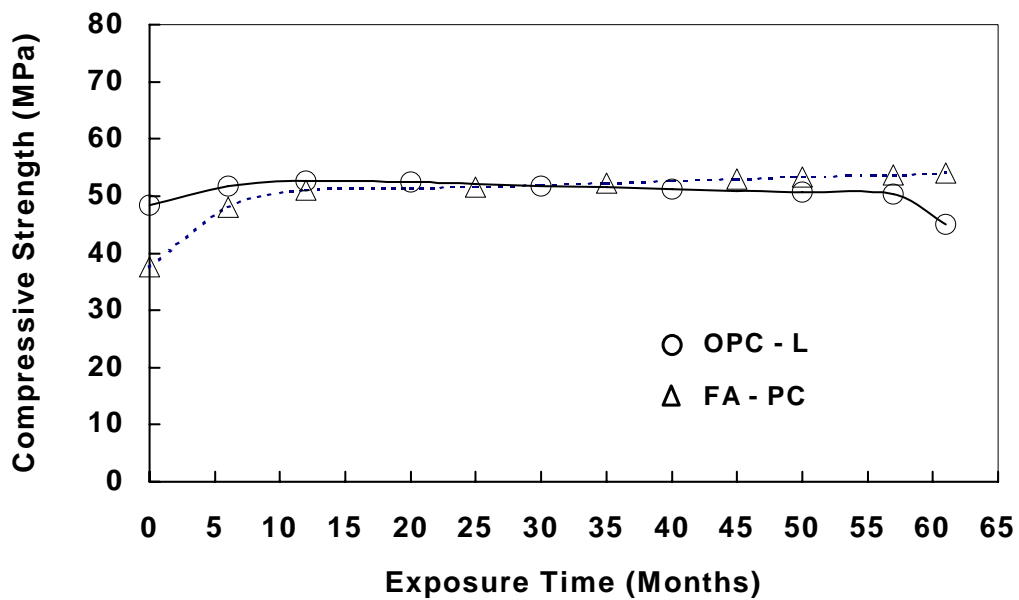


Fig. 7 – Compressive strength of mortar specimens ($w/cm = 0.55$), with limestone sand as a function of cement type ($SO_4^- = 3000$ mg/l).

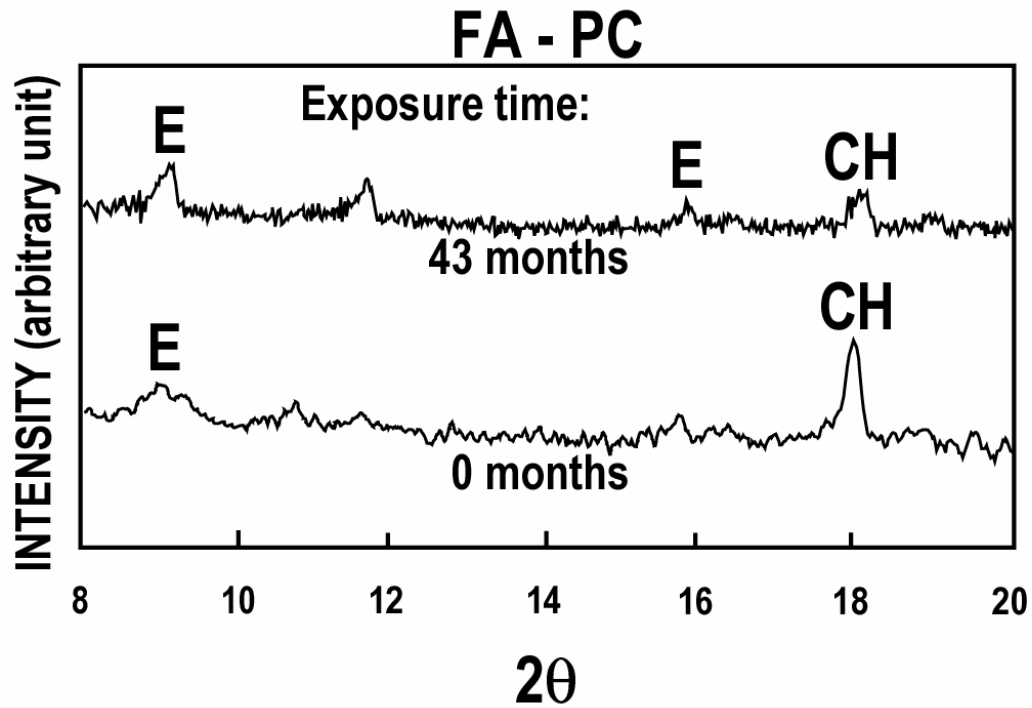


Fig. 8 – XRD pattern of surface paste specimens with fly ash-portland cement (FA-PC) before and after exposure to 3000 mg/l sulfate solution.

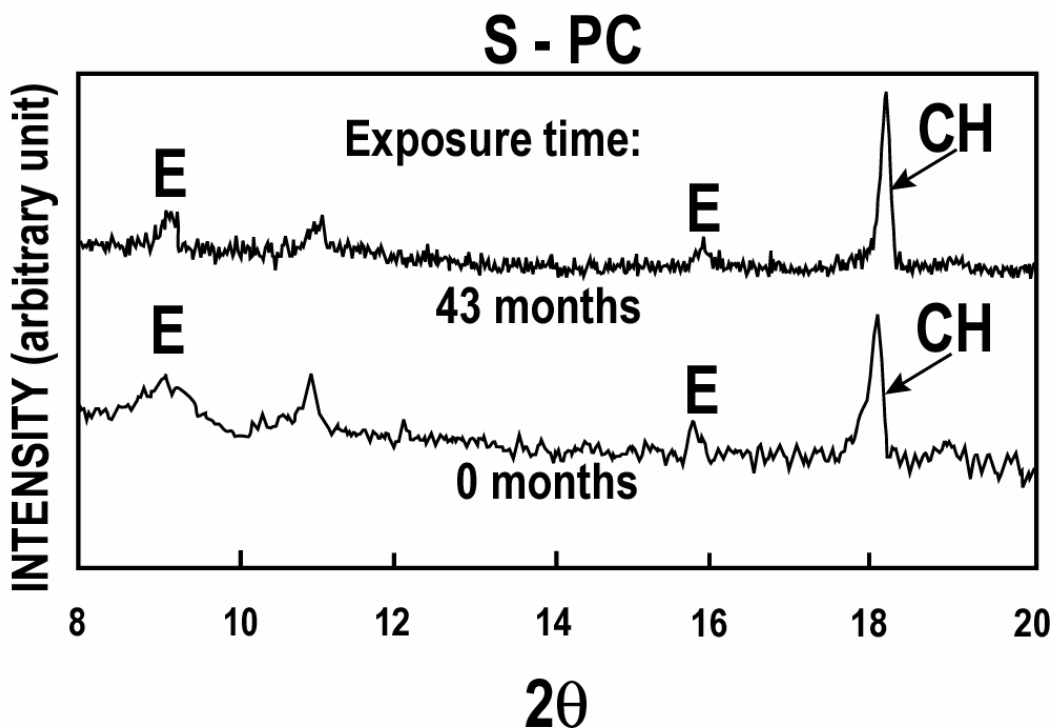


Fig. 9 – XRD pattern of paste surface specimens with slag-portland cement (S-PC) before and after exposure to 3000 mg/l sulfate solution.

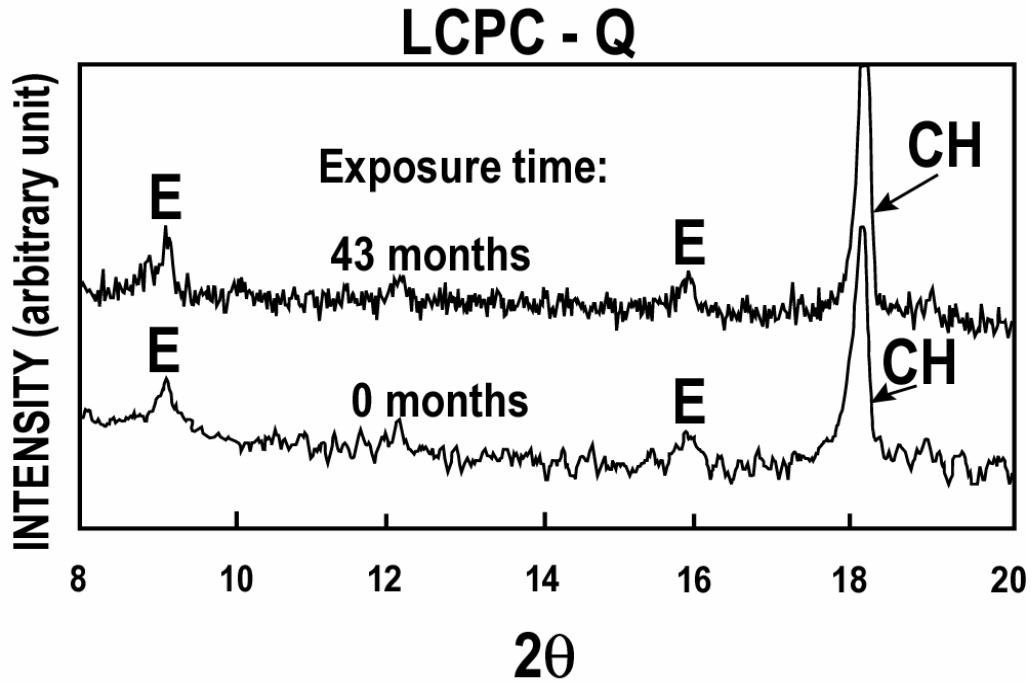


Fig. 10 – XRD pattern of surface paste specimens with C_3A -free portland cement and siliceous filler (LCPC-Q) before and after exposure to 3000 mg/l sulfate solution.

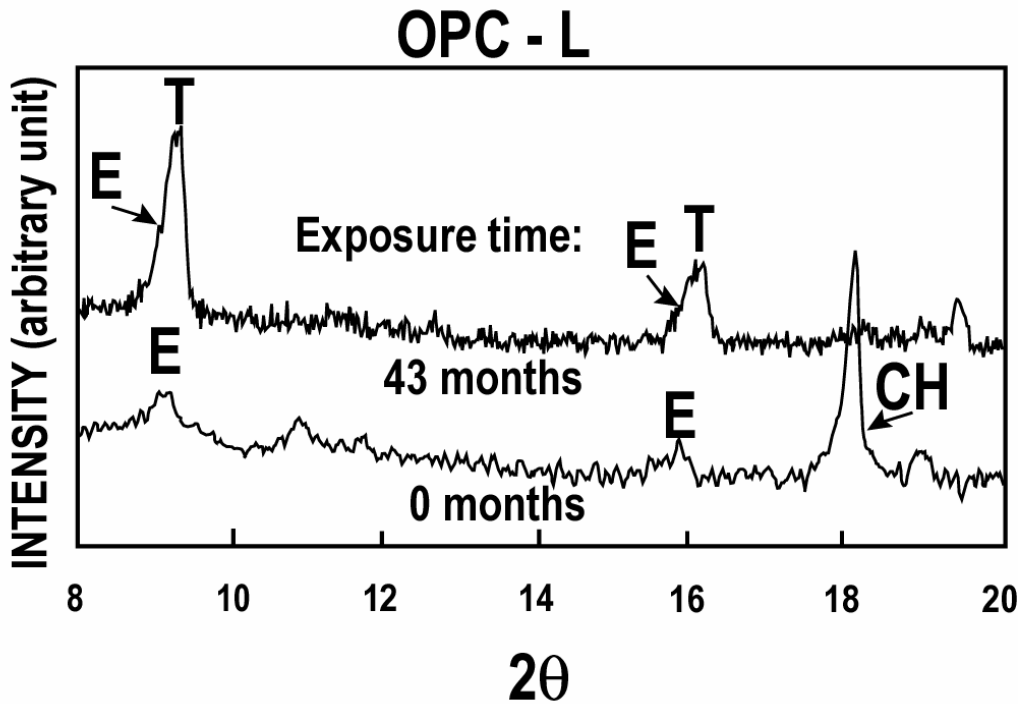


Fig. 11 – XRD pattern of surface paste specimens with ordinary portland cement and limestone filler (OPC-L) before and after exposure to 3000 mg/l sulfate solution.

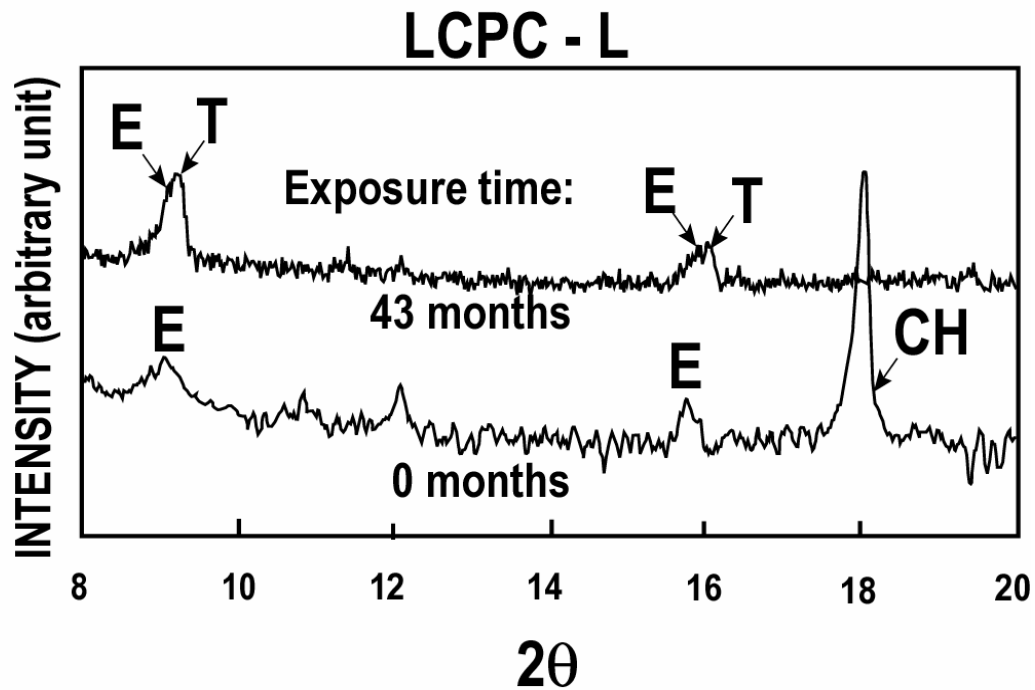


Fig. 12 – XRD pattern of surface paste specimens with C_3A -free portland cement and limestone filler (LCPC-L) before and after exposure to 3000 mg/l sulfate solution.

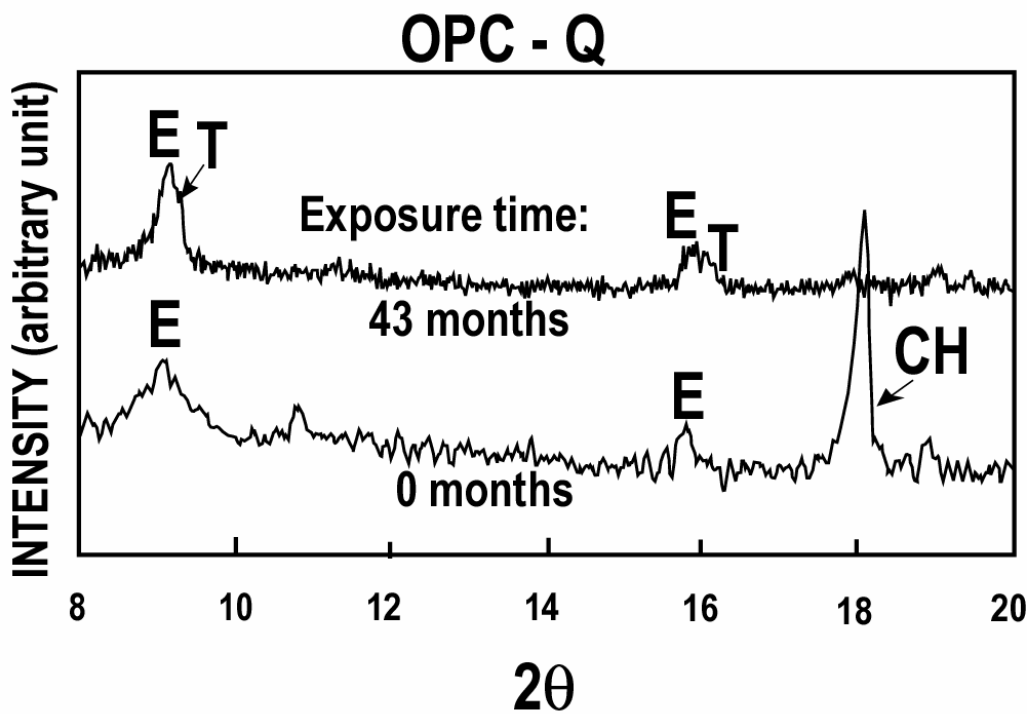


Fig. 13 – XRD pattern of surface paste specimens with ordinary portland cement and siliceous filler (OPC-Q) before and after exposure to 3000 mg/l sulfate solution.

Keywords: Durability, Sulfate Deterioration, Ettringite, Thaumasite
Limestone Blended Cements.